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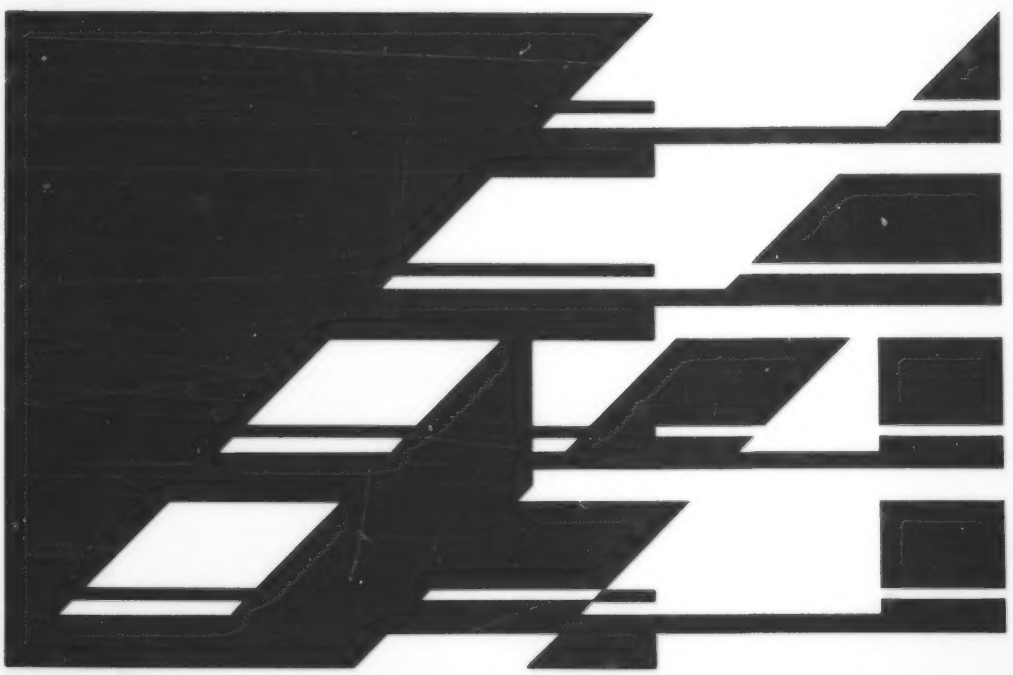

# DEVELOPMENT OF MONITORING AND PROCESS CONTROL EQUIPMENT FOR USE IN GOLD CYANIDATION

**FOR**

**CANADA CENTRE FOR MINERAL AND ENERGY TECHNOLOGY**

**ENERGY MINES AND RESOURCES**

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# ABSTRACT



The thesis of this paper is to develop a measurement system which can be used in monitoring several hydrometallurgical variables simultaneously so as to provide information in studying the kinetics and thermodynamic properties of the reactions (i.e., gold cyanidation). The first part of the paper presents the basic functions of the μMAC-6000 measurement system and how the measurement devices interface with the μMAC-6000 system. Special attention has been given to the pH measurement. Because of the high resistance of the glass electrode, the use of direct measurement method for reading out the electrode potentials is not feasible. A modified pH electrode with a built-in operational amplifier is found to be able to interface with the μMAC-6000 system. In the cases of dissolved oxygen and gas flowrate measurements, direct measurement methods are applicable on both oxygen electrode and gas flow meter. The second part is to apply the measurement system developed in the previous section to monitor an oxidation reaction of ferrous ion. The results encourage further research on the measurement system and show the need for better equipment design.

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# 1. INTRODUCTION

The leaching of gold ores in cyanide solution is a common extraction method used in gold processing. The current gold cyanidation process lacks in a developed process control strategy. To ensure the effectiveness of the process, dissolved oxygen content in the cyanide solution is kept at saturation level by over supply of oxygen gas. However, the dissolution of gold is very slow and leads to a very significant consumption of cyanide and oxygen. The optimization of gold cyanidation, is therefore, a very important aspect for increasing gold recovery and decreasing operating costs.

Before proceeding in controlling and optimizing the leaching process of gold, it is essential to develop a measurement system which can provide reliable information of the process. The μMAC-6000 data acquisition system, manufactured by the Analog Devices Company, is used as a central unit for simultaneous measurement of several variables. The objective of this project is to interface the μMAC-6000 system with the following measurement devices: oxygen electrode, mass flow meter, pH electrode, and thermocouple so as to develop a measurement system to monitor an oxidation reaction.

The development of this project is divided into two parts: i) instrumentation and ii) application. In the part of instrumentation, the data acquisition system is interfaced with various measurement devices, and the correlation curve of individual devices is obtained. Because of safety restrictions attached to cyanide use, application of the system developed in part (i) will be based on the iron (II) oxidation reaction in $H_2SO_4$ in the presence of a cupric catalyst.

## 2. INSTRUMENTATION

μMAC-6000 system, which is a Modular I/O Processor designed to measure and control a broad range of industrial processes, is implemented with an IBM AT compatible (PHILIPS P3202) as a host computer. The schematic of the key components is shown in Figure 1. The μMAC-6000 system serves as a bridge in between the host computer and various measurement devices. The analog signals picked up from the measurement devices are fed simultaneously into the μMAC-6000 system. The analog signals are then digitized and shown on the host computer.[1] The measurement devices consist of oxygen electrode, pH electrode, mass flow transducer and mass flow meter, and thermocouple. Special attention has been given to interfacing the electrodes, particularly the pH electrode, because low level measurement is encountered.

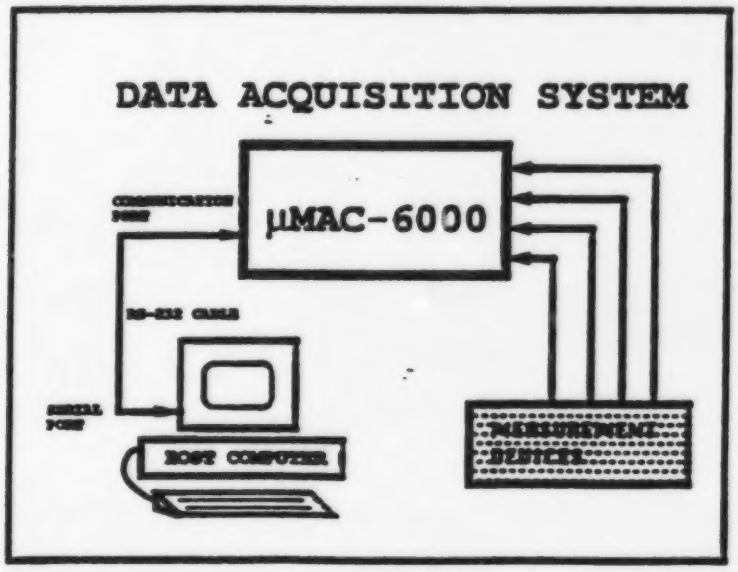


**Figure 1.** **Three key components of the Data Acquisition System (DAS).**

## 2.1 COMMUNICATION BETWEEN μMAC-6000 SYSTEM AND HOST COMPUTER

An asynchronous RS-232C communications cable is used to connect the serial port COM1 of the μMAC-6000 system to COM1 of the host computer. The μMAC-6000 system configuration should be set as follows:

System Console (SC) = 1
Program Development (PD) =1
Baud rate = 9600
No parity, 8 data bits, 1 stop bit.[2]

A communication software WOS which is run on the host computer is required to establish the communication between μMAC-6000 system and host computer. The WOS software also enables the host computer to be used as a development system for programming the μMAC-6000 system.[3] The programming language used is called μMACBASIC.[4] A sample program which is written to instruct the data acquisition system in monitoring several physicochemical variables simultaneously is presented in APPENDIX A.

## 2.2 pH MEASUREMENT

An epoxy-bodied gel-filled pH electrode (model number PHE-1304) which is a product of the OMEGA Company is used. Direct interface between the electrode and μMAC-6000 system is performed. A 5B41-01 module in μMAC-6000 system which has an impedance of 200 megaohms and an input range of +/- 1V is selected for reading the electrode potentials while the pH electrode is immersed in a known pH buffer solution. Figure 2 and 3 are the results recorded from μMAC-6000 system when the electrode is in pH 5 and pH 7 buffer solutions, respectively. Both figures show that the output voltages are fluctuating. This measurement problem arises because the resistance across the glass electrode bulb is as high as 100 megaohms, the module which does not have an impedance high enough could draw appreciable current from the electrode and cause a voltage drop across the electrolyte and polarize the cell. To accurately determine the potential of the pH electrode, a device which has a high input impedance and low bias current is required.[5,6]

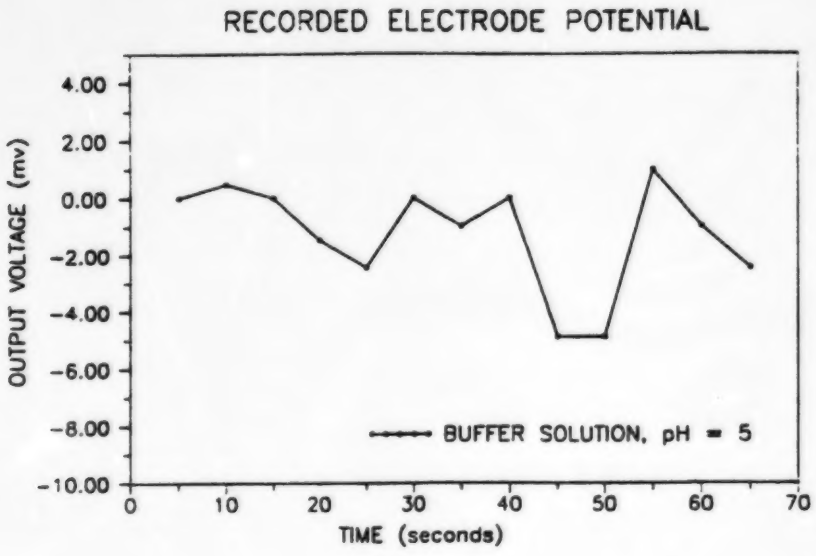


**Figure 2.** Electrode potential of the pH electrode in pH 5 buffer solution recorded by the µMAC-6000 system.

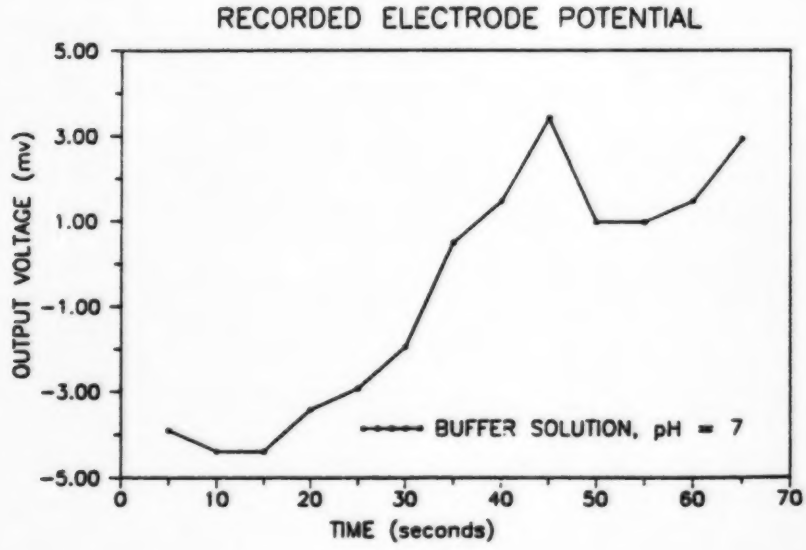


**Figure 3.** Electrode potential of the pH electrode in pH 7 buffer solution recorded by the µMAC-6000 system.

pH electrode can be modeled as a mV-level voltage source with a high internal resistance. It is therefore important to have an amplifier with a very low input bias current such that the voltage drop due to current drawn by the amplifier does not become significant in terms of a pH unit. A monolithic electrometer operational amplifier (model number AD549J, Analog Devices Company) with input bias current of 150 fA and input impedance of $10^{13}$ ohms is used. A circuit diagram is drawn in Figure 4.[7] Because of the time constraint, the circuit has only been developed to a point that the output signals from the modified pH electrode can be read from a FLUKE multimeter; however, the development stage of the circuit is not mature enough to have the electrode directly interface with the μMAC-6000 system. Since pH is dependent on temperature, to accurately determine the pH a temperature compensation network should be added to the basic pH electrode amplifier. The temperature compensated pH electrode amplifier consists of three components: an AD549 amplifier, an AD590 temperature compensator, and an AD535 analog divider, and is shown in Figure 5.[8]

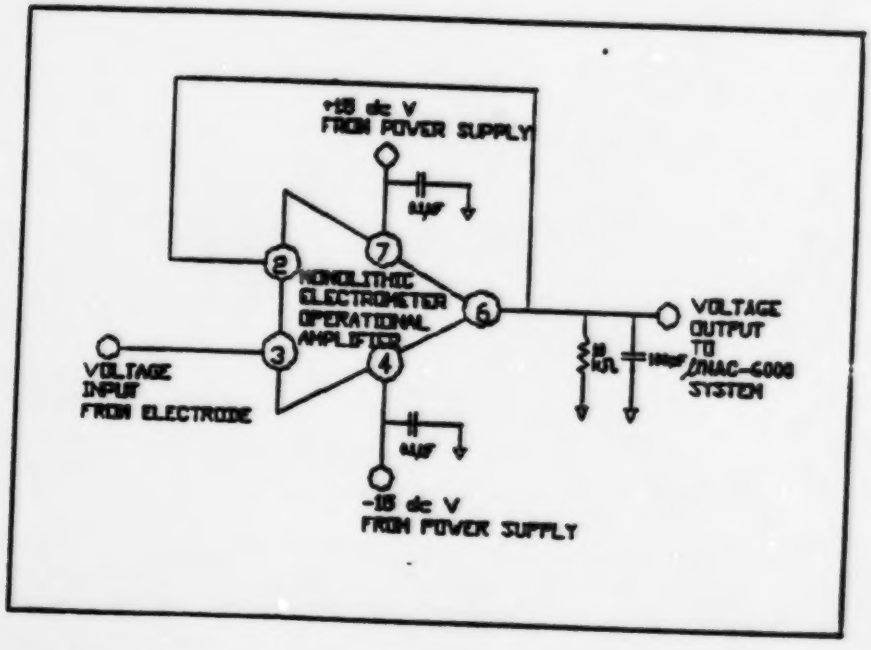


Figure 4. Circuit diagram of a monolithic electrometer operational amplifier.

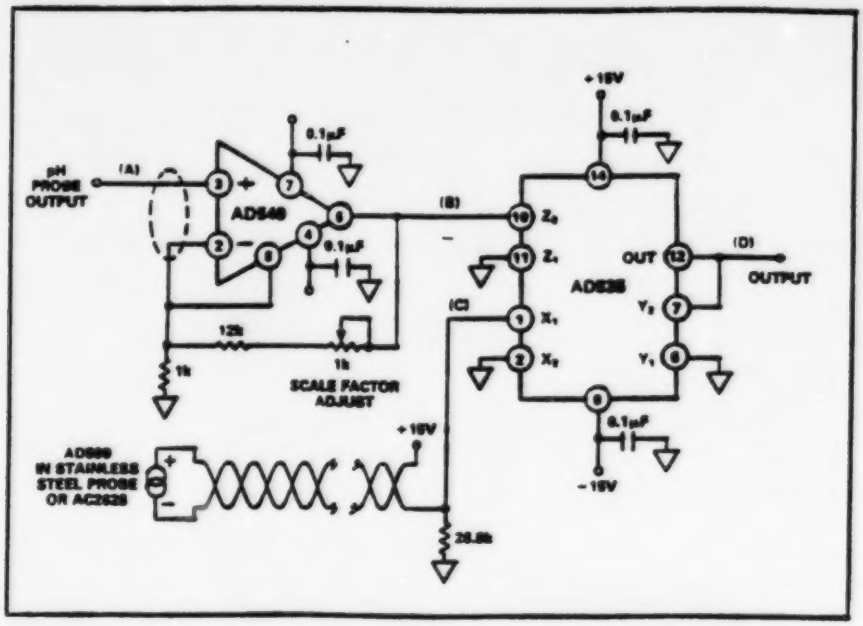


Figure 5. Temperature compensated pH electrode amplifier.

Recently, the OMEGA Company has developed a pH electrode (model number PHE-1304-EB) with an amplifier built-in. The electrode is successfully interfaced with the μMAC-6000 system. The correlation graph of electrode potential versus pH at 23°C is plotted in Figure 6. The calibration equation is represented by:

$$e = -57.80\ pH + 401.5 \qquad (1)$$

where e is the electrode potential read from the μMAC-6000 system. For a solution temperature of 23°C, Figure 6 shows that the electrode potential changes by 57.80 mV/pH and the asymmetry potential is at 6.95 pH. Analytically, electrode potential can be related to pH by simplifying the Nernst equation to:

$$e = 0.1984(T + 273.16)(7 - pH) \qquad (2).$$

For a solution temperature of 23°C, Eq.(2) shows that the electrode potential changes by 58.76 mV/pH and the asymmetry potential is at 7 pH. The experimental values agree to the theoretical with 1.6% error.

pH measurement accuracy depends on bias, span, and linearity errors from variety of sources. Typically, under the best of industrial conditions, pH electrode potential measurements are not more accurate than about +/- 1 millivolt or +/- 0.017 pH. The drift of asymmetry potential is about +/- 0.3 millivolts per day or +/- 0.006 pH per day.[9]

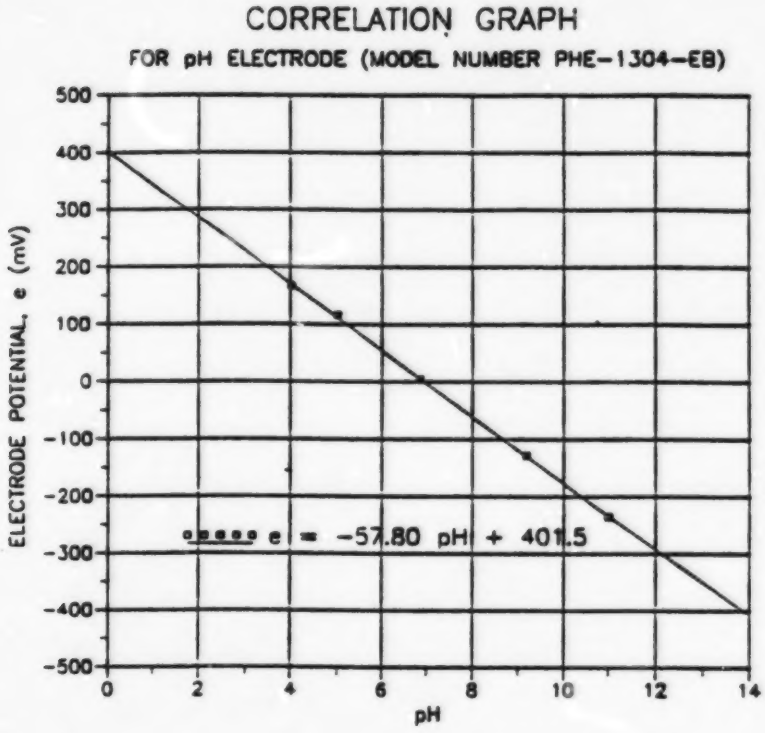


Figure 6. Electrode potential versus pH at 23.0 °C.

Glass electrodes which used for pH measurement and e.m.f. measurement are based on the electrochemical cell principle. The difficulties arise from direct measurement of the electrode potential from both pH and e.m.f. electrode are expected to be similar.The basic concept of e.m.f. methods of pH measurement and the properties of the glass electrode are presented in Appendix C.

## 2.3 INTERFACE OF OXYGEN ELECTRODE AND AIR FLOWMETER WITH μMAC-6000 SYSTEM

The Orion model 97-08 oxygen electrode is successfully interfaced with the μMAC-6000 system. Originally, the electrode is designed to be used with a pH meter. From the pH meter, dissolved oxygen concentration is read directly in parts per million or in milivolts. The two types of units are related linearly, and their relationship is expressed as:

$$C = -16.9\,u + 7.00 \qquad (3)$$

where C is oxygen concentration in ppm and u is voltage output in volts. A correlation graph is shown in Figure 7. Electrode standardization is carried out in water-saturated air. The electrode has two calibration controls: zero calibration knob is used to obtain a zero reading, and air calibration knob is used to set barometric pressure of air.[10]

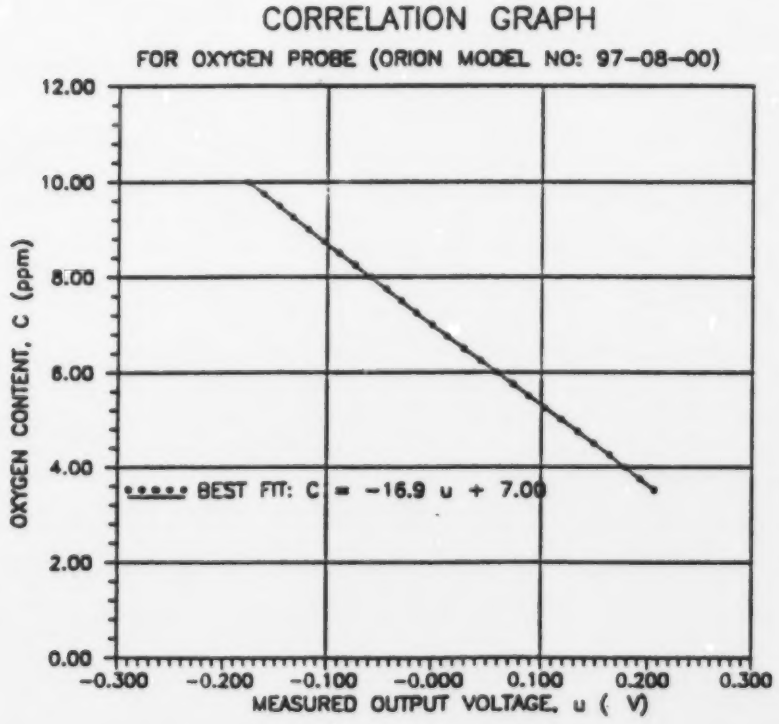


Figure 7. Calibration of dissolved oxygen content versus output voltage of the electrode.

Matheson model 8272 mass flow transducer and 8280 air flowmeter are used to regulate dry air flow rate. The transducer operates on +/- 15.0 Vdc power, provides a 0-5.0 Vdc output signal linearly proportional to the flow rate. The maximum flow allowed for the transducer is 5.0 slpm (standard litre per minute).[11] The correlation between flow rate and output signal becomes:

$$Q = m \qquad (4)$$

where Q is dry air flow rate in slpm and m is output signal in volts. The correlation graph is shown in Figure 8. The output signal from the transducer is fed into the flow meter, and from there, the signal is sent to the μMAC-6000 system.

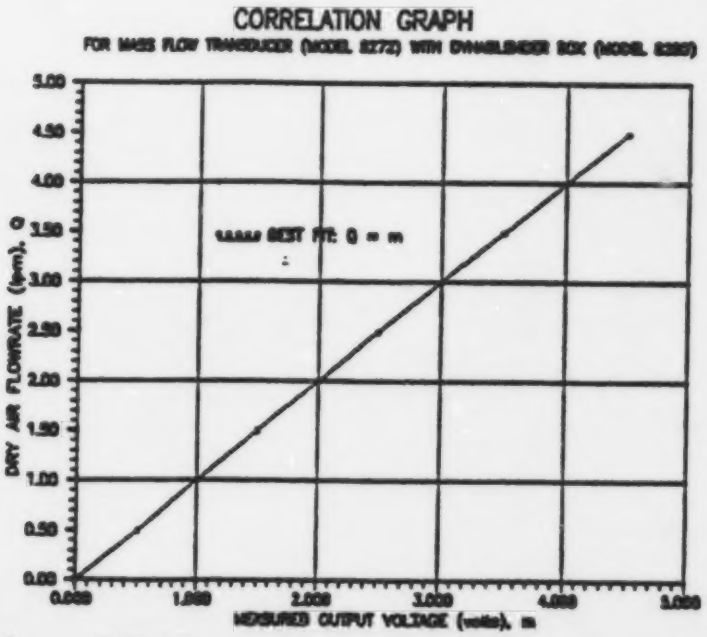


Figure 8. Calibration of air flowrate versus output voltage received from mass flow meter.

# 3. EXPERIMENTAL SECTION

The Data acquisition system developed in the previous section was used to monitor an oxidation reaction of ferrous sulphate. The reaction is written as:

$$4Fe^{2+} + O_2 + 4H^+ \text{---> } 4Fe^{3+} + 2H_20 \qquad (5).$$

The parameters of interest include dissolved oxygen concentration C, pH, supply air flow rate Q, temperature, and percent oxidation of ferrous ion.

An oxygen electrode, a pH electrode, and a K type thermocouple which were connected to the μMAC-6000 system were inserted into a reaction vessel. The reaction vessel was a 1.5-litre beaker covered with a sheet of aluminum foil. A dry air supply line with a flow rate regulator was directed into the vessel containing a litre of solution. The solution was being well agitated by a magnetic bar. The schematic of the setup is shown in Figure 9.

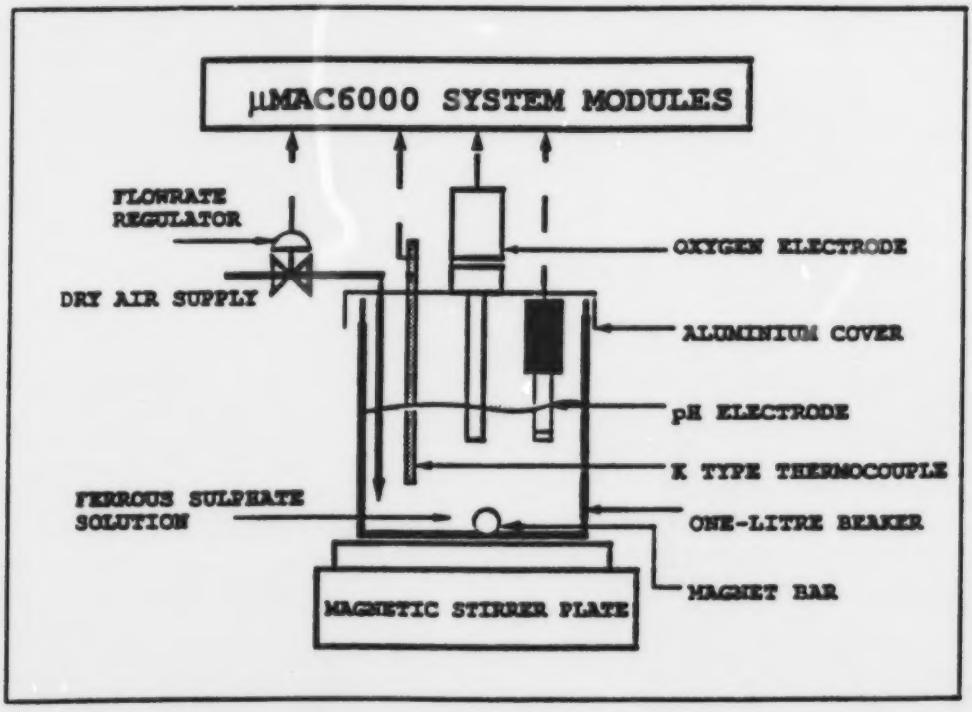


Figure 9. Schematic of the reaction vessel.

All experiments were done at room temperature,and oxygen was supplied at a constant flow rate. Ferrous ion solution with initial ferrous ion concentration of 0.10 M was prepared from ferrous sulphate ($FeSO_4.7H_2O$) and acidified to about 1.5 pH by adding 5 ml of 10 N $H_2SO_4$ solution. The solution was immediately transferred into the reaction vessel, and a portion of the initial solution was saved for titration analysis. Then 1.0 g of cupric sulphate in aqueous form which was used as a catalyst was dropped into the vessel. Simultaneous measurements began. In the beginning, no oxygen was being enforced into the solution, but oxygen was allowed to be diffused into the solution from the atmosphere. Dissolved oxygen in the solution was consumed by the oxidation reaction and was decreasing. When dissolved oxygen content dropped to an equilibrium level, bubbling of oxygen started. The reaction was continuously monitored till the solution was saturated in oxygen. Bubbling of air stopped and measurements terminated. The solution was emptied from the vessel and saved in a flask for titration analysis. A total of four experiments were conducted with same initial ferrous concentration and same amount of catalyst, but the bubbling rate of air was different for all experiments: 0.5 slpm of dry air was supplied for experiment number 1, 1.00 slpm for experiment number 2, 2.00 slpm for experiment number 3, and 4.00 slpm for experiment number 4.

## RESULTS AND DISCUSSION

The most significant variable for the experiments was dissolved oxygen concentration. For all experiments, the initial concentrations of oxygen in solution were recorded to be in a range of 7.52 to 8.44 ppm. Without any enforcement of oxygen into the solution, it took about 10 hours to obtain a minimum level of oxygen content. At this steady state, the rate of oxygen consumed by the reaction was said to be equal to the rate of oxygen diffused from the atmosphere. The minimum level of oxygen obtained in each experiment was different and was in a range of 3.90 to 5.00 ppm. When bubbling of air began, the oxygen content level was increased steeply, and the level rose by more than 3 ppm in less than 20 minutes. As air continuously being bubbled into the solution, the oxygen content increased asymptotically towards a saturation level. The saturation level in each experiment was almost different from each other, and was in a range of 7.50 to 8.20 ppm.

Because all experiments were done with diluted (0.10M) ferrous sulphate solution at room temperature, the temperature and ionic strength effect on the oxygen saturation level would not be significant. In fact, the titration analysis showed that only about 10 percent of ferrous ion was oxidized. In order to have a higher percent of oxidation, a higher reaction temperature and solution pH should be used.

Figure 11 showed the measurement of oxygen content recorded in Experiment number 2. The minimum and maximum oxygen content were found as 3.90 ppm and 7.70 ppm, respectively. In a period of 10 hours, 10 percent oxidation of ferrous ion was determined by titration analysis of initial and final solutions. Since the initial concentration of $Fe^{2+}$ was 0.10 M, 10 percent oxidation would not consume more than 0.01 mole hydrogen ion per liter of solution. Therefore, pH would increase less than 0.1 pH. From the pH curve in Figure 12, the initial and final pH were detected to be 1.268 and 1.283, respectively. Because the accuracy of the pH electrode itself was not more than 0.017 pH, this small change could not lead to any specific conclusion. To have a large impact on pH, a higher ferrous ion concentration was suggested such that the consumption of hydrogen ion in the solution would be more apparent.

The temperature curve in Figure 12 showed that the solution temperature was not kept at room temperature, but rather varied in a range of +/- 1 $^{o}$C. The main reason of this temperature variation was that the reaction vessel was not insulated, and the room temperature was badly controlled. To improve this situation, the reaction vessel should be

insulated by means of a water bath. In addition, to have a better control of the reaction condition, the reaction vessel should be well sealed to minimize disturbances from the surroundings.

Figure 13 showed the enlarged sections of the oxygen curves in a region where sharp changes of oxygen content were observed. Each curve represented a corresponding constant flow rate supply of dry air. While bubbling of dry air began, the oxygen concentration in the solution increased sharply. This implied that the rate of oxygen consumed by the oxidation reaction was substantially slower than the rate of dissolution of oxygen from the air supply line. This illustrated again the rate of reaction of the current employed reaction was too slow. To increase the rate of the reaction, a higher concentration of ferrous ion and higher solution temperature was suggested.

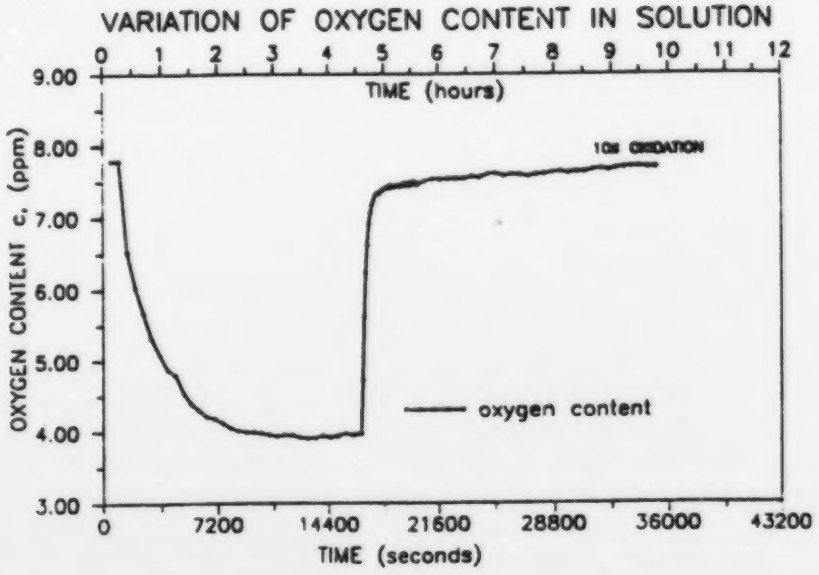


**Figure 10.** **Results from Experiment number 2; measurements of dissolved oxygen content.**

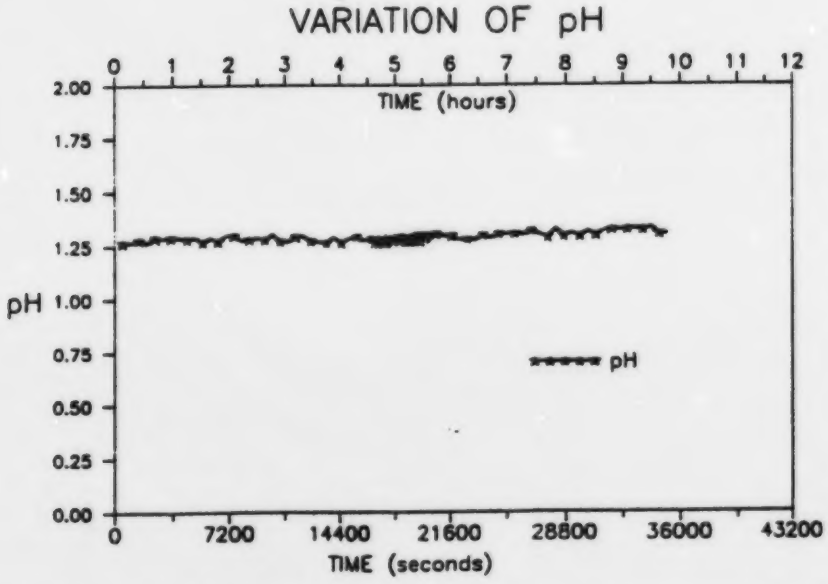


**Figure 11.** **Results from Experiment number 2; measurements of pH.**

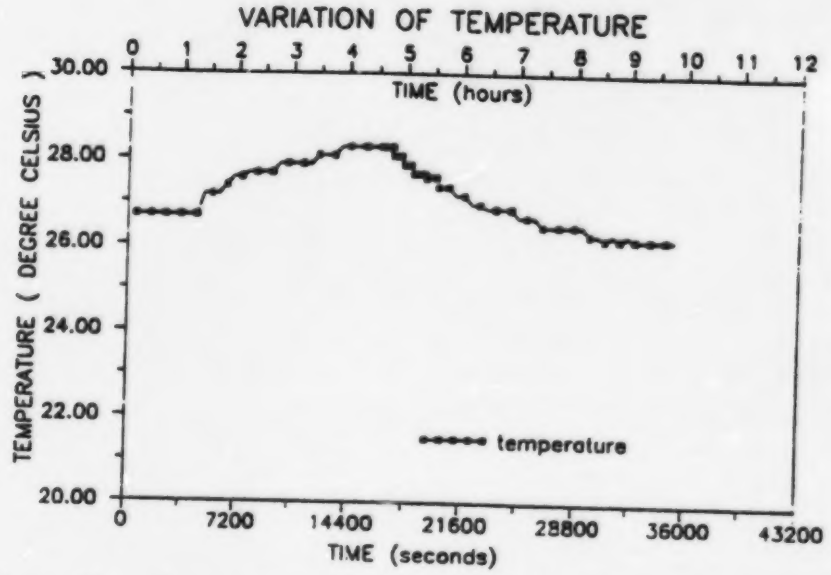


**Figure 12.** **Results from Experiment number 2; measurements of temperature.**

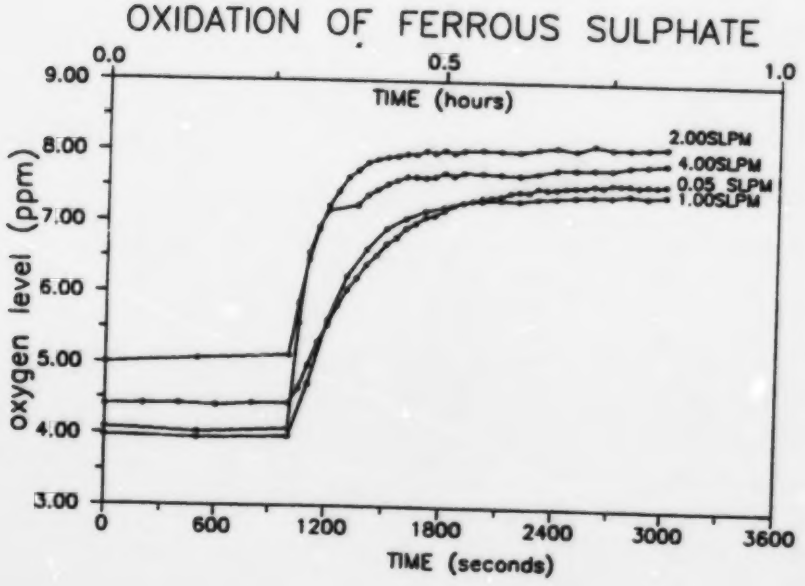


**Figure 13.** **The enlarged section of the oxygen curves showed how the dissolved oxygen content varied for different rate of air supply.**

# 5. CONCLUSIONS AND RECOMMENDATIONS

- Simultaneous measurements of dissolved oxygen content, pH, temperature, and air flowrate through the use of the μMAC-6000 system were achieved. Further testing of the reliability, accuracy, and reproducibility of the system at various conditions are encouraged.

- Addition of an amplifier to a conventional pH electrode can minimize the polarization effect caused by the high resistance of the glass bulb; and therefore, makes possible the direct measurement of electrode potential by the μMAC-6000 system. By the same principle, e.m.f electrode may be interfaced with the μMAC-6000 system.

- The reaction vessel should be sealed to minimize disturbances from the surroundings; the vessel should be placed in a water bath to ensure constant temperature.

- A solution with a high concentration (1.0M) of ferrous ion along with a high reaction temperature (45-80$^{o}$C) is suggested in order to increase the rate of consumption of oxygen and hydrogen ion in the solution. Therefore measuring of the physicochemical variable can be examined within a wider range of conditions.

# 6. NOMENCLATURE

| | |
|---|---|
| a | activity |
| C | dissolved oxygen content (ppm) |
| E | e.m.f. of the cell (V) |
| $E^0$ | standard e.m.f. of the cell (V) |
| $E_a$ | asymmetry potential of a glass electrode (V) |
| $E_j$ | the liquid junction potential (V) |
| e | pH electrode potential at 23°C (mV) |
| F | Faraday constant (96487 coulombs) |
| $\Delta G$ | Gibbs free energy (J) |
| m | voltage output from the mass flowmeter (V) |
| n | number of electrons involved in the overall reaction |
| Q | flowrate of dry air supply (slpm) |
| T | temperature of solution (°C) |
| u | voltage output from oxygen electrode (V) |
| $\mu$ | chemical potential (J) |

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Anonymous, "8280 Series Dynablender Boxes", Matheson Gas Products.

# APPENDIX A.

## A SOFTWARE USED TO DIRECT THE μMAC-6000 SYSTEM TO MEASURE SEVERAL PARAMETERS SIMULTANEOUSLY

**SAMPLE PROGRAM**

```
INTEGER: TOK, C%, Z
REAL: TOTTIME, INCRETIME
STRING: SCREEN[16], BACK[72]

Interrupt Procedure VOLTAGE
     EXTERNAL: TOK, C%

     100  REM  THIS IS A SUBPROGRAM WHICH WILL BE EXECUTED
     200  REM  ONLY IF IT IS CALLED UPON BY THE INTERRUPT
     300  REM  COMMANDS.
     400  REM  ----------------------------------------
     500  REM  IF INTERRUPT NUMBER (INTR) IS EQUAL TO 10 THEN
     600  REM  IT IS A TIME INTERRUPT THEN STORE OUTPUT AT
     700  REM  SPECIFIED TIME INTERVAL; OTHERWISE, IF INTR IS
     800  REM  EQUAL TO 11 WHICH IS A KEY INTERRUPT, THEN
     900  REM  SHOW OUTPUT ON SCREEN UPON USER'S REQUEST BY
     1000 REM  PRESSING A CORRESPONDING KEY.
     1100 IF INTR=10 THEN GOTO 1500
     1200 PRINT USING "####.#;s" TIMER
     1300 PRINT USING "##.##;slpm,##.##;ppm,pH=##.##,
     temp(°C)=###.##" Ain(101),Ain(102),Ain(103),Ain(104)
     1400 GOTO 1800
     1500 PRINT #TOK USING "####.#;sec" TIMER
     1600 PRINT #TOK USING "##.##;slpm,##.##;ppm,pH=##.##,
     temp(°C)=###.##" Ain(101),Ain(102),Ain(103),Ain(104)
     1700 C%=C%+1
     1800 PRINT,, TIMER, "READING #", C%, IS STORED"
     EXIT

     100  REM  MAIN PROGRAM
     200  REM  OPEN A OUTPUT FILE WHERE DATA WOULD BE STORED
     300  REM  INTO
     400  OPEN ("o", "OUTPUT", TOK)
     500  REM  DEFINE SYSTEM CONFIGURATION
```

```
600  SYSCONFIG (0,0,"")
700  REM  DEFINE LOGICAL CHANNELS TO PHYSICAL CHANNELS
800  ATYPE (101,0,0,8,6,4,0)
900  ATYPE (102,0,0,3,4,4,0)
1000 ATYPE (103,0,0,4,4,4,0)
1100 ATYPE (104,0,0,9,35,4,0)
1200 REM  INQUIRE THE TOTAL TIME OF MEASUREMENT AND TIME
1300 REM  INTERVAL BETWEEN MEASUREMENTS
1400 INPUT "ENTER TOTAL TIME OF MEASUREMENT (SEC)?"
TOTTIME
1500 INPUT "ENTER SAMPLING TIME INTERVAL (SEC)?"
INCRETIME
1600 REM SET TIME TO ZERO
1700 ZTIMER
1800 C%=0
1900 REM INTERRUPT COMMAND
2000 ON INTERRUPT VOLTAGE
2100 REM TIME INTERRUPT
2200 SET(10,INCRETIME)
2300 REM (ESC) KEY INTERRUPT
2400 SET(11,27)
2500 IF C%*INCRETIME <= TOTTIME THEN GOTO 2500
2600 REM CLOSE OUTPUT FILE
2700 CLOSE (TOK)
ENDFILE
```

# APPENDIX B

## SAMPLE RAW DATA COLLECTED DURING THE $Fe^{2+}$ to $Fe^{3+}$ OXIDATION

For every two row the first row indicates the time when measurement is taken (in second). From left to right, the second row shows the readings of flowrate of air supply (in slpm), dissolved oxygen content (in ppm), pH, and temperature (in $^{o}C$).

Experiment #: 4
Date:91-03-17
Data4.1

550.0
- 0.00 slpa, 7.52 ppa, 0.00 mV,pH= 1.311, TEMP 24.799316
1000.0
- 0.00 slpa, 7.32 ppa, 0.00 mV,pH= 1.308, TEMP 24.399414
1499.9
- 0.00 slpa, 6.47 ppa, 0.00 mV,pH= 1.275, TEMP 24.399414
1999.9
- 0.00 slpa, 6.06 ppa, 0.00 mV,pH= 1.294, TEMP 24.199218
2499.9
- 0.00 slpa, 5.77 ppa, 0.12 mV,pH= 1.308, TEMP 24.199218
2999.9
- 0.00 slpa, 5.49 ppa, 0.00 mV,pH= 1.260, TEMP 24.199218
3499.8
- 0.00 slpa, 5.25 ppa, 0.00 mV,pH= 1.264, TEMP 24.399414
3999.8
- 0.00 slpa, 5.10 ppa, 0.00 mV,pH= 1.294, TEMP 24.199218
4499.8
- 0.00 slpa, 4.91 ppa, 0.00 mV,pH= 1.279, TEMP 24.599609
4999.8
- 0.00 slpa, 4.81 ppa, 0.00 mV,pH= 1.302, TEMP 24.599609
5499.7
- 0.00 slpa, 4.67 ppa, 0.00 mV,pH= 1.289, TEMP 24.799316
5999.7
- 0.00 slpa, 4.59 ppa, 0.00 mV,pH= 1.297, TEMP 24.799316
6499.7
- 0.00 slpa, 4.53 ppa, 0.00 mV,pH= 1.304, TEMP 24.899414
6999.7
- 0.00 slpa, 4.46 ppa, 0.00 mV,pH= 1.308, TEMP 24.899414
7499.6
- 0.00 slpa, 4.37 ppa, 0.00 mV,pH= 1.281, TEMP 25.099609
7999.6
- 0.00 slpa, 4.32 ppa, 0.00 mV,pH= 1.262, TEMP 25.099609
8499.6
- 0.00 slpa, 4.32 ppa, 0.00 mV,pH= 1.294, TEMP 25.299316
8999.6
- 0.00 slpa, 4.29 ppa, 0.12 mV,pH= 1.302, TEMP 25.499511
9499.5
- 0.00 slpa, 4.22 ppa, 0.00 mV,pH= 1.266, TEMP 25.499511
9999.5
- 0.00 slpa, 4.19 ppa, 0.00 mV,pH= 1.256, TEMP 25.599609
10499.5
- 0.00 slpa, 4.18 ppa, 0.00 mV,pH= 1.273, TEMP 25.599609
10999.4
- 0.00 slpa, 4.13 ppa, 0.00 mV,pH= 1.285, TEMP 25.799316
11499.4
- 0.00 slpa, 4.12 ppa, 0.00 mV,pH= 1.251, TEMP 25.799316
11999.4
- 0.00 slpa, 4.12 ppa, 0.00 mV,pH= 1.260, TEMP 25.999511
12499.4
- 0.00 slpa, 4.12 ppa, 0.00 mV,pH= 1.292, TEMP 25.999511

# APPENDIX C[12]

## E.M.F METHODS OF pH MEASUREMENT

## C1. ELECTROCHEMICAL CELLS AND ELECTRODE POTENTIALS

A typical electrochemical cell consists of a solution in which two electrodes are inserted, at which the chemical action can occur if the circuit is closed to complete the system. In the system, work is done as a result of a chemical reaction. This work manifests itself as an e.m.f. which is set up within the cell, from the tendency for the reaction to proceed. If the spontaneous e.m.f. is opposed by an equal and opposite e.m.f., applied externally, the system is then thermodynamically reversible and the observed e.m.f. values are available for thermodynamic calculations. The total work which can be done by the cell is measured its change in free energy, and may be equated to the electrical energy:

$$-\Delta G = nFE$$

where n is the number of electrons involved in the overall reaction, F is the Faraday (96487 coulombs), and E is the e.m.f. of the cell. $\Delta G$, the Gibbs free energy, represents the difference in chemical potential between products and reactants:

$$-\Delta G = \sum n \mu_{products} - \sum n \mu_{reactants}$$

Since the chemical potential terms, $\mu$, involve activities, from

$$\mu_i = \mu_i^o + RT \ln a_i$$

it follows that

$$E = -\Delta G / (nF) = E^o + (RT/(nF)) \sum \ln a_i$$

where $E^o$ is a standard e.m.f. comprised of terms $\mu_i^o / (nF)$.

The total e.mf. of a simple cell can be considered to be the algebraic sum of the potential values of two half cells acting in opposition, each comprising one electrode system. The potential of each individual electrode is then given by

$$E = E^o + (RT/(nF)) \sum \ln a_i$$

which is a form of the Nernst equation.

In the case of hydrogen electrode the reaction is

$$H^+ + e^- = 1/2\ H_2$$

The activities of pure substances, solid, liquid, or gas, are defined as having unit value, so that the only variable in the reaction is the hydrogen ion activity. Then

$$E = E^o + (RT/F) \ln a_{H+}$$

which is the potential of the hydrogen electrode. $E^o$ is the potential of the electrode when $a_{H+} = 1$, usually termed the standard potential of the electrode, and is constant for a given temperature. $E^o$ represents a measure of the thermodynamic tendency for the electrode to lose or gain its ions in solution around it.

## C2. ELECTROCHEMICAL pH CELL

Electrochemical cells can be devised which will give an e.m.f. whose Nernst expression involves the hydrogen ion activity of the solution concerned. The requirements are:

(1) An indicator electrode reversible with respect to hydrogen ions.
(2) A reference electrode, whose e.m.f. is unaffected by the changes in the composition of the cell solution, or whose e.m.f. is affected in a predictable way.
(3) Finally, apparatus for measurement of the cell e.m.f. is needed. It is important that no current, or only a negligible amount, be drawn from the cell, since otherwise thermodynamic reversibility will be destroyed and e.m.f. will alter. Consequently an e.m.f. must be applied so as to compensate for the cell e.m.f. exactly, as in the Poggendorff method. Although potentiometers can be used, the widespread use of high resistance glass electrodes demands some form of amplification to detect the e.m.f. nullpoint in the balanced system; this is provided by commercial 'pH meter'.

## C3. PROPERTIES OF GLASS ELECTRODE

When a glass electrode is placed in contact with a solution, a potential will be set up across the glass-solution boundary according to the Nernst equation if a true pH response property exists:

$$E = E^{o} - (2.3026\ RT/F)\ pH$$

This equation implies that at a given temperature the measured e.m.f should be a linear function of pH, the slope having the value -2.3026 RT/F. However, glass electrodes do not function linearly in e.m.f. response over the entire pH range, and a considerable amount of work has been directed towards the measurement of so-called 'alkaline error' and to its minimization. The alkaline error is e.m.f. deviation to more positive millivolt values in high pH solutions than theoretically required. This positive e.m.f. error causes a pH lower than the true value to be observed. Furthermore, sluggishness is observed in reaching an equilibrium value even at pH values in the region 0-2 when a glass electrode is transferred to a low pH solution from a higher one.

In the use of a glass electrode for continuous measurement of pH, a property of fundamental importance is the speed of response. A time interval between change of medium and change of e.m.f. can be expected where diffusion to electrode surface is slow, for any of a number of possible reasons. It is also possible that exchange equilibration at the electrode surface may not be instantaneous, but it is not easy to separate a factor of this kind from the diffusion one. The electrical time constant measurable with a glass electrode regarded as a capacitor would ideally exclude diffusion effects; a calculation on a glass electrode of 200 MΩ resistance and 10 mm diameter bulb gives a time constant of about 40 msec. A caution on possible instrumental effects should be noted. pH amplifiers incorporate, in some manner, a capacitance, which may be in the form of a capacitor at the electrode input stage. In some instruments a relatively large capacitor may be connected, on which charge adjustment has to be made to achieve equilibrium. This constitutes an additional time constant factor, but one which is not normally significant. However, when certain electrode glasses having marked dielectric absorption properties (lithium glasses, for example) are used, significant time lags can occur with a high instrument capacitance. A charge adjustment has to be made, and the time taken appears to be a function of the dielectric absorption coefficient, the instrument capacitance, and the e.m.f. change.

## C4. TEMPERATURE CHARACTERISTICS OF pH ELECTRODE

The measurement of pH by e.m.f. methods is profoundly subject to temperature factors, as can be seen from the e.m.f.-pH relationship of a pH cell. The Nernst equation, modified to include the liquid junction potential, $E_j$, and the asymmetry potential of a glass electrode, $E_a$, gives

$$E = E^o + E_a + E_j + (2.3026\ RT/F)\ pH$$

This relationship indicates the possible sources of temperature variation in the measured e.m.f.-true pH relationship. These are apart from true pH, which are in principle independent of the technique of measurement. All four terms on the right-hand- side of the equation can be considered temperature-dependent and all must be taken into account in measuring pH by e.m.f. methods.

The slope of linear e.m.f.-true pH curve is equal to 2.3026RT/F. If a pH metering device is calibrated directly in pH units, it is desirable that some means be available to allow for the change of slope factor with temperature. Most commercial electrode-meter assemblies do provide means for manual or automatic temperature compensation, the automatic ones utilizing a wire-wound thermometer or thermistor. The electrical resistance of these compensators varies with temperature, the resistance being applied in the feedback circuit.

Full temperature compensation requires that allowance be made for variation with temperature of the true pH of the sample as well as zero shift and the slope factor. This is not generally practical,because of variation in pH-temperature coefficients from one solution to another. Where, however, a solution has virtually a constant composition and consequently its true pH-temperature coefficient is constant and can be determined, this may be incorporated into the pH of the cell.